Orthogonalising pseudo-potentials in scattering calculations

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Abstract

The Orthogonalising Pseudo-Potential (OPP) introduced by Kukulin and Krasnopolsky is applied to scattering problems. Two simple models admitting analytic solution were used to illustrate the behaviour of the scattering states as a function of the OPP strength parameter. These were a system with a zero-range potential having one bound state, and free particle scattering subject to an orthogonality constraint. Application of the OPP to electron scattering from helium in a modified static exchange model, and Ps scattering from He in an s-wave model, were used to demonstrate that the results derived from the model-potential analysis are also valid in a numerical calculations.

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1. Introduction

Some of the major difficulties in formulating the electron–atom scattering problem arise from the antisymmetric nature of the wave function. From a computational point of view the exchange interaction is more difficult to evaluate than the direct interaction. While the evaluation of the exchange interaction matrix elements tends to slow down any calculation, they do not lead to unsurmountable difficulties and the exchange interaction is routinely included in calculations of electron scattering.

A much more sinister set of problems arises from the consideration of the Pauli principle. It is known that two electrons cannot occupy the same state described by a full set of space and spin quantum numbers. This leads to numerous problems in the application of the close coupling ansatz to the description of electron–atom scattering. It is known that the antisymmetrized electron–atom close-coupling equations may not have unique solutions [1]. It was demonstrated that this nonuniqueness of the close coupling equations could lead to numerical instabilities and degrade the reliability of the numerical solutions [2].

One remedy for the problem was the imposition of orthogonality constraints in addition to the usual scattering boundary conditions. The very successful and widely used R-matrix program uses Lagrange orthogonalization [3] to construct a set of continuum orbitals that are orthogonal to the orbitals used to construct the target wave
functions. The use of an orthogonal continuum basis in turn led to an additional set of problems [4] which have only recently been circumvented [5,6].

The problems that arise in r-space close coupling equations also arise when the close-coupling equations are written in terms of a set of momentum space Lippmann–Schwinger (LS) equations. These problems were highlighted and solved for a number of systems in a series of papers by Stelbovics and collaborators [7–9]. The essential problem of the CC equations in LS form was the fact that the half-shell T-matrix was not uniquely defined. Although the on-shell T-matrix amplitudes were uniquely defined, they could become unstable in a numerical solution of the LS equations. Stable solutions of the LS equations were derived by using projection operators and making appropriate modifications to the exchange kernel. This work has been of crucial importance to the development and success of the Convergent Close Coupling (CCC) method [10].

In this work we describe the application of the Orthogonalized pseudo-potential (OPP) to the treatment of electron–atom scattering problems. The Orthogonalized pseudo-potential (OPP) method was first introduced by Krasnopolsky and Kukulin [11,12] in the context of nuclear physics and has recently been used extensively in calculations of exotic positron–atom bound states [13–15]. A detailed computational investigation of the application of the OPP in bound state calculations has recently been published [16].

Despite the fact that it can be shown that OPP method has quite a rigorous foundation in scattering theory [11], there has not been a detailed investigation illustrating the use of this method for a practical scattering problem. In the present manuscript, the main features of the OPP procedure when applied to scattering problem are illustrated on an example of a simple model system having one bound state. Following this, a numerical investigation of the use of the OPP is made for some simple scattering systems.

2. The orthogonalized pseudo-potential method

The problem to be solved is the Schrödinger equation for positive energies

\[ \hat{H} |\Psi\rangle = E |\Psi\rangle \]  (1)

with the constraint that certain vectors are excluded from the manifold of allowable solutions, i.e. the solution \( |\Psi\rangle \) of (1) should satisfy the constraints \( \langle \Phi_i | |\Psi\rangle = 0, \; i = 1, \ldots, N \).

One way to do this is to use a projection operator. The projection operator \( \hat{Q} \) to exclude the subspace of the Hilbert space spanned by \( N \) orthonormal vectors \( \Phi_i \) is defined

\[ \hat{Q} = 1 - \hat{P} = 1 - \sum_{i=1}^{N} |\Phi_i\rangle \langle \Phi_i| \].  (2)

The explicit inclusion of this projection operator into the Schrödinger equation gives the modified Schrödinger equation

\[ \hat{Q} \hat{H} \hat{Q} |\Psi\rangle = E |\Psi\rangle \].  (3)

In some situations this projection operator technique is easy to apply and does not increase the computational labor to any great extent. However, there are a number of circumstances where the use of Eq. (3) is impractical and anything that can be done to simplify the situation is desirable. An alternative way to treat the constrained problem (1) is to apply an orthogonalising Pseudo-Potential (OPP). The basic philosophy of the OPP as put forward by Kukulin and Krasnopolsky [11,12] is to add a penalty function to the Hamiltonian to enforce orthogonality with those orbitals to be excluded from the active space.

The penalty function added to the Hamiltonian is the projection operator \( \hat{P} \) multiplied by a constant, viz.

\[ \hat{H}_p = \hat{H} + \lambda \hat{P} \].  (4)
where
\[ \lambda \hat{P} = \sum_i \lambda_i |\Phi_i\rangle \langle \Phi_i| . \] (5)

When constant \( \lambda \) is chosen so that it is large and positive, it acts as a repulsive potential and effectively excludes any component of the set \( \{|\Phi_i\rangle\} \) from the solution [11]. In the limit of large \( \lambda \) the solution of Eq. (4) reduces to that of the solution of the constrained Schrödinger equation (1). The OPP potential has been recently exploited in frozen core calculations of positron binding atoms [15] and a detailed computational investigation of the properties of solution vectors as a function of \( \lambda \) has been published recently [16].

The formal expression for the \( T \)-matrix of the scattering process for the Hamiltonian (4) can be obtained at once with the help of the Gellman–Goldberger two potential formula [17]
\[ T_{\alpha,\beta}(\lambda) = T_{\alpha,\beta}(0) + \lambda \langle \Psi^-_{\beta} | \Phi \rangle \langle \Phi | \Psi^+_{\alpha} \rangle \langle \Phi | (E - \hat{H} - \lambda \hat{P})^{-1} (E - \hat{H}) | \Phi \rangle . \] (6)

In this expression, \( \alpha, \beta \) stand for the quantum numbers describing scattering states, \( |\Psi_{\alpha}^\pm\rangle \) are energy normalized scattering states of the Hamiltonian \( \hat{H} \) with outgoing (+) and in (−) boundary conditions, \( \Phi \) is an excluded vector. The value of \( T_{\alpha,\beta}(0) \) coincides with the \( T \)-matrix for the Hamiltonian \( \hat{H} \).

One situation that can be encountered occurs when it is wished to exclude some of the bound eigenstates of the Hamiltonian. Modifications introduced by the penalty function (5) are trivial in this case, provided the vectors \( |\Phi_i\rangle \) are exact eigenvectors of \( H \). Another case occurs when the states to be excluded are approximate but not exact eigenstates of the scattering Hamiltonian. This is the case that typically occurs in electron–atom scattering. The eigenstates to be excluded are the solutions of an \( N \)-electron Hamiltonian, while the scattering problem involves an \( N+1 \)-electron Hamiltonian. A very simple example would be static-exchange scattering of electrons from helium (i.e. the scattering potential consists of the direct and exchange interactions of the scattering wave function with a Hartree–Fock target wave function). Inclusion of anti-symmetry could be done by using the OPP method (with \( |\Phi_i\rangle \) taken as the Hartree–Fock ground state 1s orbital. While the formal solution of the problem is given by Eq. (6), this equation does not give much insight into the use of the OPP method since it gives little detailed information into the behaviour of the OPP solutions as a function of \( \lambda \). More insight into the behaviour of the OPP solutions can be obtained by investigating simple model problems and this is now done.

3. OPP for the model problems

3.1. OPP for free motion

This model is trivial, but even this simplest case illustrates features that can be seen in more realistic scattering calculations. It could be noted that this model is not devoid of physical interest since it describes the construction of a constrained orthogonal basis that can be useful in the scattering theory [18,19].

Suppose the solution of the Schrödinger equation for free motion is sought orthogonal to the vector \( g(r) = (2\mu)^{1/2} \exp(-\mu r) \) normalized so that \( \int_0^\infty g^2(r) \, dr = 1 \). The solution of the Schrödinger equation of the OPP free Hamiltonian requires the solution of the integro-differential equation
\[ R''(r) + k^2 R(r) = 4\lambda \mu e^{-\mu r} \int_0^\infty e^{-\mu x} R(x) \, dx \] (7)

with the usual boundary condition \( R(0) = 0 \). This equation can be solved by the use of a Laplace transform. For the wave function and the \( K \)-matrix the following expressions can be easily obtained
\[ R(r) = \sin kr + \frac{4\mu \lambda}{k^2 + \mu^2 - 2\lambda} \left( e^{-\mu r} - k \cos kr + \mu \sin kr \right) \frac{\mu^2 + k^2}{\mu^2 + k^2} , \] (8)
\[ K_{\lambda P} = -\frac{4\mu k}{(k^2 + \mu^2)^2/\lambda + 2(\mu^2 - k^2)}. \]  

(9)

In the limit of large \( \lambda \), the \( K \)-matrix takes the form

\[ K_{\lambda P} \sim -\frac{2\mu k}{(\mu^2 - k^2)} \left( 1 - \frac{(k^2 + \mu^2)^2}{2\lambda(\mu^2 - k^2)} + O(\lambda^{-2}) \right). \]  

(10)

The \( K \)-matrix decreases with increasing \( \lambda \) with a \( O(1/\lambda) \) correction to the limiting value.

### 3.2. OOP for zero-range potential

A more interesting example of the OOP formalism is provided by the zero-range potential since this system exhibits many of the salient features of a real scattering system but is sufficiently simple to permit exact solution.

The solution of any scattering problem can be characterized by the logarithmic derivative \( c \) of the wave function \( R(r) \) for any radius \( (r) \) larger than the radius of the potential \( (r_s) \). A zero-range potential has the unique property that the logarithmic derivative is independent of energy [17]. The Schrödinger equation for the zero-range potential is that of a free particle with the asymptotic boundary condition imposed on the logarithmic derivative of the wave function

\[ R''(r) + k^2 R(r) = 0, \quad \lim_{r \to 0} \frac{R'(r)}{R(r)} = -c. \]  

(11)

The parameter \( c \) is a characteristic of the model-potential. The solution of the unconstrained zero-range Schrödinger equation have the following properties. The potential affects only \( s \) waves. The \( s \)-wave, \( K \)-matrix and phase shift are given by

\[ R(r) = \sin(kr + \delta), \quad K = \tan \delta = -\frac{k}{c}. \]  

(12)

For positive \( c \) the system has one bound state with the energy \(-c^2/2\) and the normalized wave \((2c)^{1/2} \exp(-cr)\).

Now consider the constrained scattering problem for this model. Suppose the solution is sought orthogonal to the vector \( g(r) = (2\mu)^{1/2} \exp(-\mu r) \). When the parameter \( c \) in Eq. (11) is positive and \( \mu = c \) the excluded vector describes the bound state of the system.

In the projection operator formalism Eq. (3), the solution of the constrained problem reduces to solution of the inhomogeneous equation

\[ R''(r) + k^2 R(r) = v g(r), \quad \lim_{r \to 0} \frac{R'(r)}{R(r)} = -c, \]  

(13)

where the parameter \( v \) is determined by the orthogonality requirement and is

\[ v = \frac{-2 \sin(\delta) \mu (\mu - c)}{\sqrt{2\mu}}. \]  

(14)

The wave function is

\[ R(r) = \sin(kr + \delta) - \frac{2 \sin \delta \mu (\mu - c)}{k} \left( k e^{-\mu r} - k \cos kr + \mu \sin kr \right), \]  

(15)

where \( \delta \) is given by Eq. (12). The \( K \)-matrix which defines the asymptotic phase, \( K_{\Omega \Omega} \) in Eq. (15) is

\[ K_{\Omega \Omega} = -\frac{k}{c} \frac{3\mu^2 + k^2 - 2\mu c}{c^2 - \mu^2 + \frac{2\mu^3}{c}}. \]  

(16)

For positive \( c \) and \( \mu = c \) (i.e. exclusion of the exact eigenstate of \( \widehat{H} \)) Eqs. (15) and (16) reduce to the corresponding expressions (12) for the unconstrained problem.
The solution of the Schrödinger equation of the OOP Hamiltonian requires the solution of the integro-differential equation

\[ R''(r) + k^2 R(r) = 4\lambda \mu e^{-\mu r} \int_0^\infty e^{-\mu x} R(x) \, dx, \quad \lim_{r \to 0} \frac{R'(r)}{R(r)} = -c. \]  

(17)

This can be solved by using Laplace transform techniques giving the following expressions for the wave function and \( K \)-matrix

\[ R(r) = \sin(kr + \delta) + \frac{2 \sin \delta}{k} \frac{2\lambda \mu (\mu - c) \cdot ke^{-\mu r} - k \cos kr + \mu kr \sin kr}{\mu^2 + k^2} \]  

(18)

and

\[ K_{\lambda P} = -\left(\frac{k}{c}\right) \frac{3\mu^2 + k^2 - 2\mu c}{k^2 - \mu^2 + \frac{2\mu^2}{c}} \frac{\lambda - \lambda_c}{\lambda - \lambda_o} = K_{OHQ} \frac{\lambda - \lambda_o}{\lambda - \lambda_c}. \]  

(19)

The parameters \( \lambda_o \) and \( \lambda_c \) in (19) are given by

\[ \lambda_o = \frac{(\mu^2 + k^2)^2}{2(k^2 - \mu^2 + 2\mu^2/c)}, \]  

(20)

\[ \lambda_c = \frac{(\mu^2 + k^2)^2}{2(k^2 - 2\mu c + 3\mu^2/c)}. \]  

(21)

An immediate consequence of Eqs. (19), (20) and (21) is that \( K_{\lambda P} \to K_{OHQ} \) when \( \lambda \to \infty \). This is compatible with the formal analysis [11]. We also note that \( K_{\lambda P} \) can never be equal to \( K_{OHQ} \) for a finite value of \( \lambda \) unless \( \mu = c \). It is instructive to look at the limiting behaviour of \( K_{\lambda P} \) at large \( \lambda \); this is given by

\[ K_{\lambda P} = K_{OHQ} \left(1 + \frac{\lambda_c - \lambda_o}{\lambda}ight) + O(\lambda^{-2}). \]  

(22)

It is seen that \( K_{\lambda P} \) approaches \( K_{OHQ} \) as \( O(1/\lambda) \) with the size of the coefficient depending on the difference between \( \mu \) and \( c \).

It is interesting to track the behaviour of \( K_{\lambda P} \) as a function of \( \lambda \) from \( 0 \to \infty \). At \( \lambda = 0 \) the OOP \( K \)-matrix coincides with the phase of the nonconstrained problem. At small energies, considerations based on Levinson’s theorem suggest the threshold phase shift be set to \( \pi \). As \( \lambda \) increases, the \( K \)-matrix (and phase shift) starts to decrease (it becomes more negative). The \( K \)-matrix passes through the pole (the phase shift goes through \( \pi/2 \)) at \( \lambda = \lambda_c \). Shortly after passing through the pole, the \( K \)-matrix also has a zero at \( \lambda = \lambda_o \). Fig. 1 which is drawn for the model system with \( c = 1, \mu = 0.8 \) at \( k = 0.1 \) shows the typical behaviour of \( K_{\lambda P} \) versus \( \lambda \).

When \( \mu \approx c \), the behaviour \( K_{\lambda P} \) versus \( \lambda \) exhibits almost no change except for a small region near \( \lambda_c \) where \( K_{\lambda P} \) changes abruptly. When \( K_{\lambda P} \) is plotted versus \( \lambda \) for \( \mu \approx c \) the graph looks rather uninteresting as within the thickness of the line, one gets a perfectly straight horizontal line with a vertical line appearing at the transition region. The difference in position of the pole and the zero when \( \mu \approx c \) is

\[ \lambda_c - \lambda_o = O(\mu - c)^2. \]  

(23)

which shows that the width of the transition region decreases quickly as \( \mu \to c \). The position of the transition region for \( \mu \approx c \) is given by

\[ \lambda_c = \frac{(\mu^2 + k^2)^2}{2(k^2 - \mu^2 + 2\mu^2/c)} = \frac{(\mu^2 + k^2)^2}{2} \left(1 + \frac{2\mu^2(1 - \mu/c)}{(\mu^2 + k^2)} + \ldots \right). \]  

(24)
Fig. 1. Tangent of the phase shift for the one-level system, \( c = 1, \mu = 0.8 \) at \( k = 0.1 \) (solid line) as a function of \( \lambda \). The dashed line denotes the value of \( K_{QHQ} \).

\[ \frac{K_{\lambda P} - K_{QHQ}}{K_{QHQ}} = \frac{-\mu(c - \mu)^2}{\lambda c} + \mathcal{O}(\lambda^{-2}) \]  

as \( \lambda \to \infty \). The rate at which \( K_{\lambda P} \) trends to \( K_{QHQ} \) does not depend on the kinetic energy.
The excluded state is generally not an eigenstate of $\hat{H}$ and this causes the $K_{\lambda P}$ to be different from the $K$-matrix one gets ($K = -k/c$) without any consideration of the projection. The difference between $K_{\lambda P}$ and $K$ as a function of $\lambda$ can be deduced from Eqs. (12) and (19) and

$$
\frac{K_{\lambda P} - K}{K} = \frac{2\mu(\mu - c)^2}{c(\mu^2 - k^2) - 2\mu^2} + O(\lambda^{-1})
$$

(26) as $\lambda \to \infty$. The difference between $K_{\lambda P}$ and $K$ is proportional to $(\mu - c)^2$, i.e. the effect is smaller when the excluded state is closer to being an eigenstate. The impact of the projection also decreases as the energy increases. This conclusion is illustrated in Fig. 3, where the behaviour of $(K_{\lambda P} - K)/K$ as function of $\lambda$ is shown for $c = 1$, $\mu = 0.8$ at $k = 0.1$ and $k = 1$.

Besides examining the behaviour of the $K$-matrix it is also desirable to determine the extent of the overlap between the OPP projected function and the excluded vector $g(r)$ as a function of $\lambda$. The overlap between the function $R(r)$ and $g(r)$ was computed with $R(r)$ normalized to $C' \sin(\delta \lambda)$. When this is done the normalization constant that should be used to multiply Eq. (18) is

$$
C = \frac{2}{\sqrt{1 + \frac{2N}{k^2 + \mu^2}(\mu^2 \sin 2\delta - \mu^2 \sin^2 \delta) + \frac{N^2 \sin^2 \delta}{k^2 + \mu^2} \frac{1}{k^2 + \mu^2}}},
$$

(27) where $N$ is given by

$$
N = \frac{4\lambda \mu (\mu - c)}{\mu^2 + k^2 - 2\lambda}.
$$

(28)

The overlap integral between the normalized scattering wave and the excluded vector $g(r) = (2\mu)^{1/2} \exp(-\mu r)$ is written as

$$
\langle \Psi_{\lambda P} | g \rangle = \frac{k(\mu - c)}{\sqrt{c^2 + k^2 - 4c \mu + 4 \mu^2} \sqrt{(\lambda - \lambda_1)^2 + B^2}},
$$

(29)

where

$$
\lambda_1 = \frac{k^4 + 3k^2 \mu^2 + c^2(k^2 - \mu^2) + c(2\mu^3 - 2k^2 \mu)}{2(c^2 + k^2 - 4c \mu + 4 \mu^2)},
$$

(30)

and

$$
B = \frac{k(\mu - c)^2 \mu}{c^2 + k^2 - 4c \mu + 4 \mu^2}.
$$

(31)
Fig. 4. The expectation value of the projection operator, \( \langle P \rangle \) for the one-level system, \( c = 1, k = 0.1, \mu = 0.8 \) as a function of \( \lambda \) in the transition region.

Fig. 5. The expectation value of the projection operator, \( \langle P \rangle \) as a function of \( \lambda \) for the one-level system, \( c = 1, k = 0.1, \mu = 0.8 \) (solid line), \( \mu = 0.98 \) (long dash) \( \mu = 0.998 \) (very short dash).

Fig. 4 shows the behaviour of the the expectation value of the projection operator \( \langle P \rangle \) (i.e. the square of Eq. (29)) as a function of \( \lambda \). The parameters of the model system were \( c = 1, k = 0.1, \mu = 0.8 \). The expectation shows a sharp peak near \( \lambda = \lambda_1 \), and is small everywhere else. When the excluded vector is close to the true bound state (i.e. \( \mu \approx c \)) then the width of the peak is proportional to \( (\mu - c)^2 \) and the amplitude is inversely proportional to \( (\mu - c) \). Generally, \( \lambda_1 \) is different from the point \( \lambda_c \) at which the phase passes through \( \pi/2 \), but

\[
\lambda_1 - \lambda_c = O(\mu - c)^2 \tag{32}
\]

when \( |\mu - c| \) is small.

The behaviour of \( \langle P \rangle \) at larger values of \( \lambda \) is shown in Fig. 5 for \( c = 1, k = 0.1 \) with \( \mu = 0.8, \mu = 0.98 \) and \( \mu = 0.998 \). Once \( \lambda \) is larger than the critical value \( \lambda_c \), the value of \( \langle P \rangle \) tends to decrease monotonically as \( O(1/\lambda^2) \).

Using Eqs. (29) and (30) the asymptotic behaviour of the overlap integral for large \( \lambda \) is

\[
\langle \Psi_\lambda | g \rangle \approx \frac{1}{\lambda} \frac{k(\mu - c)}{\sqrt{c^2 + k^2 - 4c\mu + 4\mu^2}} \quad \lambda \to \infty \tag{33}
\]

and the \( O(1/\lambda^2) \) behaviour of \( \langle P \rangle \) automatically follows.
The general behaviour of the model problem for finite scattering energy can be summarized as follows. At small values of \( \lambda \), there is a residual overlap between the scattering wave function and the excluded state which depends on the extent to which the excluded vector \( g(r) \) approximates an eigenstate of the Hamiltonian. As \( \lambda \) increases, the extent of the overlap increases, until \( \lambda \) reaches a critical value. Once this critical value of \( \lambda \) is exceeded, it becomes energetically unfavorable for the scattering wave function to possess this component which is rapidly expunged as \( \lambda \to \infty \).

While this analysis has been done for a zero-range potential, the results should be true in more general circumstances. The analysis for these more general situations is presented now.

### 3.3. Short-range potential

The analysis above for the zero-range potential should be applicable in the case of a short-range potential which could be considered as a zero-range one. If \( r_s \) is the range of the short-range interaction (i.e. the region where potential is finite), and \( E_{bs} \) is the energy of the bound state supported by this interaction, then the short-range interaction can be treated as a zero-range one provided \( r_s \sqrt{|E_{bs}|} \ll 1 \). Many of the results for the OOP phase shift can be expressed in terms of characteristic parameters of the short-range interaction provided the inequality is satisfied. To do so it can be noted that for the parameters \( \mu \) and \( c \) used above to characterize zero-range interaction and excluded state the following equality holds

\[
(\mu - c)^2 = -8E_{bs}(1 - \langle P \rangle_{bs}),
\]

where \( E_{bs} = -c^2/2 \) is energy of the bound state of the zero-range potential, and \( \langle P \rangle_{bs} \) is the expectation value of the projection operator (2) calculated with the bound state wave function \( (2c)^{1/2} \exp(-cr) \) of the short-range interaction. Expanding Eqs. (20) and (21) in powers of \( \mu - c \), retaining only the terms up to \( (\mu - c)^2 \) and expressing all the quantities in terms of characteristics of the potential and expectation value of the projection operator the following results for the parameters \( \lambda_c \) and \( \lambda_o \) of (20) and (21) can be obtained

\[
\lambda_c = E - E_{bs} + 4\frac{E_{bs}(E_{bs} + 3E)}{E - E_{bs}}(1 - \langle P \rangle_{bs}) + O[(1 - \langle P \rangle_{bs})^2],
\]

\[
\lambda_o = E - E_{bs} + 4\frac{E_{bs}(3E_{bs} + E)}{E - E_{bs}}(1 - \langle P \rangle_{bs}) + O[(1 - \langle P \rangle_{bs})^2],
\]

where \( E \) is the kinetic energy of the projectile. These formulas together with Eq. (19) provide a description (assuming the excluded state is similar to the bound state of the system so \( \langle P \rangle_{bs} \approx 1 \)) of the \( \lambda \) behaviour of the OOP phase for a short-range interaction, provided \( r_s \sqrt{|E_{bs}|} \ll 1 \).

### 4. Model calculations for realistic systems

Application of the OOP formalism to the realistic cases would require of course a more elaborate procedure than solving a single ordinary differential equation. The aim of this section is to illustrate the behaviour of the OOP when it is incorporated into the scattering Hamiltonian for a number of scattering systems.

#### 4.1. Model static exchange scattering from helium

In this section the results of numerical investigations performed upon the electron–helium system are presented. The calculations were carried out in the static-exchange approximation which only permits elastic scattering from the helium ground state which is assumed to be inert (the target ground state was represented by a Hartree–
Fig. 6. The behaviour of $K_{\lambda P}$ as function of $\lambda$ (in Hartree) for electron scattering from helium in the static-(local) exchange-polarization model. The incident momentum is $k = 0.3a_0^{-1}$. The dashed line denotes the value of $K_{QHQ}$.

Two sets of calculations using the Kohn variational method were performed. In the Kohn-variational calculation, the wave function is expanded as

$$\psi = \sum_i A_i \chi_i + A_s \phi_s + A_c \phi_c.$$  \hspace{1cm} (37)

The functions $\chi_i$ are short-range basis functions while $\phi_s$ and $\phi_c$ are functions that have the asymptotic form $\sin(kr)$ and $\cos(kr)$, respectively. The short-range basis and continuum basis functions can be orthogonalized to the helium $1s$ orbital, $\phi_{1s}$, so that

$$\langle \chi_i | \phi_{1s} \rangle = 0, \quad \langle \phi_s | \phi_{1s} \rangle = 0, \quad \langle \phi_c | \phi_{1s} \rangle = 0.$$  \hspace{1cm} (38)

When this is done, the effective Hamiltonian is $|\phi_{1s}\rangle \hat{H} |\phi_{1s}\rangle$. The other approach to this problem is to use basis functions which are not orthogonal to the $\phi_{1s}$ orbital and use the OPP to construct a wave function which satisfies $\langle \psi | \phi_{1s} \rangle = 0$.

No exchange-overlap terms were included in the calculation using $\hat{H}_L$. These overlap-exchange terms normally arise since the core and valence single electron states are not orthogonal and involve matrix elements such as $\langle \chi_i \phi_{1s} | (\hat{H} - E) | \phi_{1s} \chi_i \rangle$. Terms such as these should normally be included in a calculation when the scattering states have nonzero overlap with the fully occupied target states. However the inclusion of $\lambda \hat{P}$ operator means that these terms can be omitted provided that $\lambda$ is large enough.

The actual calculation performed was not an exact static-exchange calculation. The exact exchange interaction was replaced by a local interaction,$$V_{LX}(r) = -8.0r \exp(-3.1r)$$  \hspace{1cm} (39)

which gives phase shifts equivalent to the exact interaction for the $L = 0$ and $L = 1$ partial wave at $k = 0.3a_0^{-1}$.

Fig. 6 shows a comparison of $K_{\lambda P}$ and $K_{QHQ}$ for static exchange scattering of electrons for helium at $k = 0.3a_0^{-1}$. It is clear that $K_{\lambda P}$ is converging towards $K_{QHQ}$ as $\lambda$ increases. At $\lambda = 10$ Hartree, the difference between the two calculations was 0.1% while at $\lambda = 10^2$ the difference was 0.001%. The pole in the $K$-matrix occurs at about $E = 0.451$ Hartree since the bound state of the local exchange potential occurs at $E = -0.4047$ Hartree.

One feature worth noting is the small difference, about 2.5%, between $K_{\lambda P}$ at $\lambda = 0$, namely $-0.4768$ and $K_{QHQ}$ which was $-0.4658$. Similar small differences between $K_{\lambda P} = 0$ and $K_{QHQ}$ have been noticed in other test calculations performed on physical systems. This suggests that the error in ignoring the influence of the Pauli
principle while performing calculations on atomic systems is not large. Previously, Bartschat and Bray [22] ignored Pauli exclusion effects in a CC type calculations of electron-sodium scattering. The use of a simplified exchange kernel lead to hardly any discernible effect in the alignment and orientation parameters.

Close coupling calculations for the OPP Hamiltonian were also performed for the static-exchange scattering of electrons from hydrogen in the triplet channel. The results, which are not reported here in any detail confirmed that the phase shifts do not change when arbitrary amounts of the \( H(1s) \) wave function are added to the scattering wave function [7,8]. The \( K \)-matrices \( K_{\lambda P} \) and \( K_{QHQ} \) were the same to better than 7 significant digits for all values of \( \lambda \) except very close to the point of the singularity.

4.2. Ps-atom scattering

One of the more intractable scattering problems in atomic physics is the positronium–atom scattering problem. Even the simplest one-channel model, the static-exchange model represents a formidable challenge. In the static exchange-model the positronium (Ps) ground state is allowed to scatter from the field of an inert target atom with no consideration given to excitation of the target or projectile.

The inclusion of the anti-symmetry into the calculations involves two sources of difficulty. The first involves the evaluation of the electron–electron exchange matrix element between electrons in the target and the electron forming part of the Ps projectile. The other issue derives from the fact that the basis states used to represent the wave function of the Ps projectile are not orthogonal to the states of the target. This greatly complicates the evaluation of the kernel of the scattering equations. The use of the OPP can greatly reduce the complexity of the kernel.

In the case of static-exchange scattering of Ps-atom scattering, the scattering equation is written in Lippmann–Schwinger form as

\[
\langle k' | \Phi_{1z} | k \Phi_{1z} \rangle = \langle k' | \Phi_{1z} | V | k \Phi_{1z} \rangle + \int d^3k' \frac{\langle k' | \Phi_{1z} | V | k' \Phi_{1z} \rangle \langle k' \Phi_{1z} | T | k \Phi_{1z} \rangle}{E - E_{\beta'} - \frac{E_{\beta'}^2}{2} + i0},
\]

(40)

where \( V \) is the nonlocal interaction between the atomic target and \( \Phi_{1z} \) is the Ps ground state.

In terms of a QHQ approach, one way to incorporate the Pauli principle is to solve the Schrödinger equation with orthogonality constraints \( \langle \Phi | \alpha_{\text{core}} \rangle = 0 \), where \( |\alpha_{\text{core}}\rangle \) describes any core orbital. In terms of the OOP approach, the model Hamiltonian should be modified by inclusion of the projection term, which in coordinate representation can be written

\[
\lambda \hat{\mathcal{P}} = \lambda \delta (r_0 - r_i^0) \sum_{i \in \text{core}} |\alpha_i\rangle \langle \alpha_i|,
\]

(41)

where summation includes all core orbitals, \( r_0 \) is a positronic coordinate, and the delta function on the right-hand side of (41) reflects the fact that the projector does not directly affect the positron motion.

It is necessary to include into the formalism only the matrix elements \( \langle \beta' \mathbf{k}' | P | \beta \mathbf{k} \rangle \) where \( |\beta \mathbf{k}\rangle \) is a state of a free positronium in a state \( \beta \) with center of mass momentum \( \mathbf{k} \). The simplest way to compute this matrix element is to rewrite it as

\[
\langle \beta' \mathbf{k}' | P | \beta \mathbf{k} \rangle = \sum_{i \in \text{core}} \int \langle \beta' \mathbf{k}' | \alpha_i \mathbf{q} \rangle \langle \alpha_i \mathbf{q} | \beta \mathbf{k} \rangle \, d^3q,
\]

(42)

which reduces to

\[
\langle \beta' \mathbf{k}' | P | \beta \mathbf{k} \rangle = \sum_{i \in \text{core}} \int \Psi_{\alpha_i}(\mathbf{k}' - \mathbf{q}) \Phi_{\beta'}^{*}(\frac{1}{2} \mathbf{k}' - \mathbf{q}) \Psi_{\alpha_i}(\mathbf{k} - \mathbf{q}) \Phi_{\beta}(\frac{1}{2} \mathbf{k} - \mathbf{q}) \, d^3q,
\]

(43)

where \( \Psi_{\alpha_i}(\mathbf{v}) \), \( \Phi_{\beta}(\mathbf{u}) \) stand for the Fourier transforms of core orbital and positronium wave-functions, respectively.
After partial wave decomposition the matrix element reduces to the form (notation of [20,21] has been used)

\[ P_{\beta' L'}^{(J)}(k', k) = \sum_{n c L c} \int V_{\beta' L' \alpha n c L c}^{(J)} (k', q) V_{\alpha n c L c \beta L}^{(J)} (q, k) q^2 \, dq, \]  

(44)

where \( V_{\beta' L' \alpha n c L c}^{(J)} (k, q) \) is a partial wave decomposition of an overlap integral of a positronium state \( \beta' \) moving with momentum \( k \), and a state with an electron in a core orbital \( \alpha n c \) coupled to a free positron with momentum \( q \). These matrix elements can be calculated by adapting procedures described in [20,21]. The subsequent \( q \) integration in Eq. (44) does not pose serious problems.

4.3. Ps–He scattering in an s-wave model

Fig. 7 shows the behaviour of the phase shift a function of \( \lambda \) for a series of Ps–He model problems. The interaction potential is restricted to only include the \( \lambda \hat{P} \) interaction for the He core (taken from a Hartree–Fock wave function) and the local exchange interaction given by Eq. (39) (note the local exchange interaction had a less than 1% effect upon the phase shifts). Calculations were performed for a variety of Ps basis sets. In the first the coupled channel basis was restricted to only contain the Ps(1s) ground state. In the other calculations, the channel was augmented by one additional state, two additional states and three additional states.

One of the interesting results occurs for the one state calculation. The phase shift here shows no sign of stabilizing as \( \lambda \) is increased. The phase shift appears to be almost proportional to \( \ln(\lambda) \). Such a result is reminiscent of the situation for the exponential potential \( A \exp(-r) \) which is known to give \( \delta \sim \ln(A) \) for large \( A \) [17]. A Ps-basis with only one scattering state does not have the flexibility to give a zero overlap with the 1s core orbital. A previous investigation of the application of the OPP to bound state problems also revealed that the quality of the basis did have an impact on the ability of the calculation to achieve a zero overlap and this could have an impact upon the computed energy and rate for positron annihilation [16].

The phase shifts for the 2, 3 and 4 state basis sets shown in Fig. 7 seem to be compatible with the ideas expressed earlier. The phase shifts decrease monotonically as \( \lambda \) increases before reaching a plateau. Although this is not obvious from the graph, the phase shifts appear compatible with Eq. (10), i.e. they seem to be approaching a constant value with corrections that are roughly \( O(1/\lambda) \). As \( \lambda \) continues to increase for values larger than \( 5 \times 10^4 \), the rate at which the phase shift decreases starts to increase again. This is reminiscent of a similar effect present

![Fig. 7. The behaviour of the phase-shift \( \delta_{\lambda, P} \) for Ps scattering from He in a variety of models as a function of \( \lambda \) (in Hartree). The incident momentum was \( k = 0.410^{-1} \). The SVM phase shift was \( -1.257 \) rad at \( \lambda = 5000 \) Hartree and is almost indistinguishable from the CC(3) and CC(4) phase shifts at this \( \lambda \).](image-url)
in bound state calculations wherein the binding energy started to increase for values of $\lambda$ exceeding $10^6$ [16]. The use of excessively large $\lambda$ degrades the quality of the wave function as it attempts to satisfy a condition that is increasingly difficult to fulfill with a finite basis.

One peculiarity of the OPP approach is that the results of the calculations can be different from those of an orthodox CC type calculation with the same channel space in which the orthogonality constraints are not enforced. This is discussed in the next section.

4.3.1. The SVM method applied to Ps–He scattering

The results in the section above do not constitute the first application of the OPP ansatz to Ps-atom scattering. Recently, the fixed core variant of the stochastic variational method (FCSVM) [15,16] has been modified to handle scattering problems [23–25]. The essential idea of this approach is to diagonalize the system Hamiltonian in a large basis of square integrable states designed to provide a reasonable representation of a typical scattering state. The phase shifts and other information are then extracted from the positive energy pseudo-states by projecting them with $\Phi_{Ps}(r_0 - r_1)$ and fitting to the asymptotic form of the wave function, i.e. $\sin(k |r_0 + r_1| + \delta)$, at large distances from the nucleus. A full description of the method has been given recently [23–25]. This method can give phase shifts of about 1–2% accuracy for a problem like Ps–He scattering.

A number of groups have used different methods to study Ps–He scattering [25,26] and there is some consensus about the value of the scattering length when the helium atom is treated as inert. A Ps-channel space including only $L = 0$ Ps states gives a scattering length of about 1.90$a_0$ while the use of a very large Ps-basis gives about 1.82$a_0$ [26]. However, the $T$-matrix Ps–He calculation discussed in the previous section gives a scattering length of about 3.35$a_0^{-1}$.

It is possible to construct a FCSVM model of Ps–He scattering which is effectively equivalent to a large CC basis of $L = 0$ Ps states. When this is done the FCSVM calculation also gives a scattering scattering length of 3.33$a_0^{-1}$. However, when the FCSVM calculation is enlarged to give a close to exact solution of the model scattering problem, a scattering length of 1.80$a_0$ is obtained [27]. The FSCVM scattering lengths showed no systematic variation when $\lambda$ was varied between $10^2$ and $10^4$. So one has the seeming conundrum that a fully antisymmetric calculation without projection has different phase shifts than a finite channel solution using the OPP ansatz. However, when the channel space is enlarged sufficiently to give a very accurate description of the scattering wave function then the two different approaches give phase shifts which agree.

This seemingly different scattering length obtained by the OPP method for the restricted channel calculation is a manifestation of the lack of flexibility in the channel space. Effectively, a basis with only $L = 0$ Ps states is limited in its ability to drive the $\langle \lambda \hat{P} \rangle$ expectation to zero. In these circumstances, the inclusion of the $\lambda \hat{P}$ operator can have a noticeable impact upon the phase shifts. Effectively, the solutions of Eq. (4) and the $\lambda \to \infty$ solution using Eq. (5) only coincide exactly when the solution technique can satisfy $\langle \lambda \hat{P} \rangle = 0$. The OPP operator is best used in situations where it is feasible to use a sufficiently large channel space so that the $\langle \lambda \hat{P} \rangle$ expectation can be sufficiently close to zero.

5. Discussion and conclusions

The OPP method of Kukulin of Krasnopolsky [12] has been analytically examined in two limiting cases, a constrained Schrödinger equation with $V = 0$ and a zero-range potential. It has been shown that the OPP procedure will produce phase shifts that converge to those of the $\hat{Q} \hat{H} \hat{Q}$ Hamiltonian with a $O(1/\lambda)$ correction factor. One significant feature of this work was the demonstration that the Pauli forbidden states are largely purged from the scattering wave function once the OPP strength parameter $\lambda$ exceeds a certain critical value, $\lambda_{\text{crit}}$ that is approximately equal to sum of the kinetic energy and largest single particle energy of any of the excluded levels.

A test calculation upon the electron–helium system revealed that considerations of anti-symmetry can be ignored provided the effective Hamiltonian for the scattering electron and the occupied level are similar. One potential
application of the OPP procedure lies in the area of electron-scattering. The inclusion of the Pauli principle in electron–atom scattering calculations using the momentum space Lippmann–Schwinger equation is nontrivial [7]. At present there exists no general procedure for doing this and it is possible the OPP method may permit some progress to be made on this topic.

Another possible area of application occurs in positron–atom or positronium–atom scattering. If the channel space includes the Ps-formation channel then one has the problem of describing the exchange interaction between the atomic (or ionic) target orbitals and Ps. One class of existing calculations deals with this by computing the overlap integrals between Ps projectile wave function and atomic orbitals. The alternative approach, which we have used in some recent calculations [23,24] and explored in the present article is to apply the OPP ansatz. When this is done, the algebraic form of the interaction Hamiltonian is simplified. However, it is important to have a close coupling expansion that is sufficiently flexible to give a close to zero value for the $\langle \lambda \hat{P} \rangle$ expectation value.

If this is not the case, then the resulting phase shifts could be different from the phase shifts obtained from the functionally equivalent calculation that evaluates exchange-overlap terms explicitly. To conclude, the OPP can sensibly be applied to the scattering of two composite objects, but it is important to ensure that the wave function is sufficiently flexible so that the expectation of the $\lambda \hat{P}$ operator can be made sufficiently small and therefore does influence the phase shifts in a manner other than reason for which it was originally introduced.

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Appendix A. Validation of OPP matrix element

In the general case, the OPP matrix element is quite complicated. Two useful tests have been devised to check the accuracy and reliability of the analytic reduction and numerical evaluation of the OPP matrix element and it is valuable to present them here.

The first one is based on the observation that the core (s-state) wave-function in Eq. (42) can be replaced by a delta-function, $\delta(r)$. The general expression for the matrix element (42) reduces to

$$\langle \beta' | \beta | k' | P | k \rangle = \frac{1}{\sqrt{\pi}} \int \Phi^*_\beta(r) \Phi^*_{\beta'}(r) \exp \left[ -\frac{i}{2} (k-k') \cdot r \right] d^3r.$$  (45)

Computation of such integrals does not pose any problems since similar integrals routinely occur in calculations of positron–atom and electron–atom scattering. An approximation for the delta-function $\delta(r)$, as $\gamma$ gets larger, the exponential approximates a $\delta$-function more closely. The matrix elements of $\hat{P}$ when the core orbital approximates were calculated by, (a) evaluating Eq. (44) explicitly for a very sharply peaked orbital, and (b) by direct evaluation of Eq. (45). Table 1 displays the $P_{\beta' L', \beta L}(k', k)$ matrix element for $\gamma = 10^3$ for a variety of Ps initial and final states. It can be seen that there is very good agreement between the matrix elements calculated using the two methods. This test can be used to verify the correctness of the matrix element evaluation for a core consisting of $s$-type orbitals. The matrix elements calculated by the two methods generally agree within 1%.

Another useful diagnostic is based on the observation that the (partial) trace of the projector operator (41) satisfies a simple relation

$$\text{Tr} \hat{P} = \int \langle \beta k | P | \beta k \rangle \, d^3k = 8 \sum_{n, l_c} (2l_c + 1),$$  (46)
After the partial wave decomposition, the trace in Eq. (46) can be written as

$$\text{Tr } \hat{P} = \sum_{n,l,L,J} (2J + 1) \int \frac{\rho^{(f)}_{n,l,\beta L} (k, k) k^2 dk}{\rho^{(e)}_{n,l,\beta L} (k, k) k^2 dk}.$$

Table 1 reports the sequence of partial sums of Eq. (47) divided by 8 for different combinations of the core orbitals. Separate calculations for a Na(2s), Na(2s, 2p), and Na(1s, 2s, 2p) core are shown. The convergence for the Na(1s, 2s, 2p) core to the expected limit of 5 is much slower than for the Na(2s, 2p) core to the expected limit of 4. The partial wave sum, Eq. (47) converges faster for core orbitals that are more radially extended. As an example of this faster convergence, the trace was also evaluated for an L = 0 core orbital that was rather extended, e.g. \((\phi_{\text{core}} \sim e^{-0.15r})\). The convergence of the trace for this extended orbital, shown in the 5th column of Table 2 was faster than in any other case.

<table>
<thead>
<tr>
<th>(\beta' - \beta)</th>
<th>(L', L)</th>
<th>(\gamma = 10^3)</th>
<th>Expression (45)</th>
</tr>
</thead>
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<tr>
<td>(1s-1s)</td>
<td>0, 0</td>
<td>0.32542</td>
<td>0.32546</td>
</tr>
<tr>
<td>(2s-1s)</td>
<td>0, 0</td>
<td>2.9595^{-3}</td>
<td>2.9681^{-3}</td>
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<td>0.28879</td>
<td>0.28861</td>
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<tr>
<td>(2p-1s)</td>
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<td>-2.8460^{-2}</td>
<td>-2.8446^{-2}</td>
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<td>0.10590</td>
<td>0.10594</td>
</tr>
<tr>
<td>(2p-2p)</td>
<td>1, 1</td>
<td>2.3588^{-2}</td>
<td>2.3645^{-2}</td>
</tr>
</tbody>
</table>

| \(J = 1\) | \(1s-1s\) | 1, 1 | 8.6182^{-4} | 8.6182^{-4} |
| \(2s-1s\) | 1, 1 | -8.2541^{-4} | -8.2587^{-4} |
| \(2s-2s\) | 1, 1 | 1.0828^{-2} | 1.0777^{-2} |
| \(2p-1s\) | 0, 1 | 9.0790^{-3} | 9.0794^{-3} |
| \(2p-2s\) | 2, 1 | -1.6350^{-4} | -1.6354^{-4} |
| \(2p-2s\) | 0, 1 | -3.3020^{-2} | -3.2987^{-2} |
| \(2p-2p\) | 2, 1 | 3.2054^{-3} | 3.2868^{-3} |
| \(2p-2p\) | 0, 0 | 0.29955 | 0.29960 |
| \(2p-2p\) | 2, 2 | -1.2109^{-2} | -1.2068^{-2} |
| \(2p-2p\) | 2, 2 | 2.8035^{-4} | 2.7750^{-4} |

| \(J = 2\) | \(1s-1s\) | 2, 2 | 2.0339^{-6} | 2.0546^{-6} |
| \(2s-1s\) | 2, 2 | -7.0262^{-6} | -7.0314^{-6} |
| \(2s-2s\) | 2, 2 | 2.3416^{-4} | 2.3422^{-4} |
| \(2p-1s\) | 1, 2 | 7.0161^{-5} | 7.0157^{-5} |
| \(2p-2s\) | 3, 2 | 8.7123^{-7} | 8.7375^{-7} |
| \(2p-2s\) | 1, 2 | -9.6311^{-4} | -9.6620^{-4} |
| \(2p-2p\) | 3, 2 | 3.8532^{-5} | 3.8266^{-5} |
| \(2p-2p\) | 2, 1 | 9.4408^{-3} | 9.4578^{-3} |
| \(2p-2p\) | 3, 1 | -2.6321^{-4} | -2.6354^{-4} |
| \(2p-2p\) | 3, 3 | 3.6653^{-6} | 3.6089^{-6} |

where the summation includes all of the core-orbitals. This test, therefore, checks the calculation for arbitrary core. After the partial wave decomposition, the trace in Eq. (46) can be written as
Table 2
Convergence of the partial sums of the series (47) divided by 8 for different orbitals of a Na⁺ core for a projectile in the Ps ground state. The second column shows the partial sum for a Na(2p) core, the third column the sum for a Na(2s,2p) core and the fourth column the sum for a Na(1s,2s,2p) core. The last column contains results for model core consisting of a very extended s-orbital

<table>
<thead>
<tr>
<th>J</th>
<th>Na(2p)</th>
<th>Na(2s,2p)</th>
<th>Na(1s,2s,2p)</th>
<th>Extended 1s</th>
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<td>3.4536</td>
<td>3.8683</td>
<td>0.8682</td>
</tr>
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<td>4.1414</td>
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</tr>
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<td>3.8645</td>
<td>4.4965</td>
<td>0.9705</td>
</tr>
</tbody>
</table>

References

[27] The FCSVM scattering length quoted here was computed using the local approximation to the core-exchange interaction. The scattering length of 1.840a₀ quoted in [23] was computed with the exact core-exchange interaction.